TRITERPENE GLYCOSIDES OF Poterium polygamun AND P. lasiocarpum

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We have studied for their content of triterpene glycosides two species of burnet: Poterium polygamum collected in the Shemakha region of the Azerbaidzhan SSR, and Poterium lasiocarpum Boiss. et Haussk, family Rosaceae, collected in the Shakhbuz region of the Nakhichevn ASSR.

The comminuted roots were extracted separately with 70% ethanol. The vacuum-concentrated aqueous ethanolic extract was treated successively with petroleum ether, chloroform, and ethyl acetate–n-propanol (4:1). The glycosides were precipitated from the aqueous extract with acetone and were fractionated on a column of KSK silica gel in the butan-1-ol–ethanol–water (1:1:1) system [1].

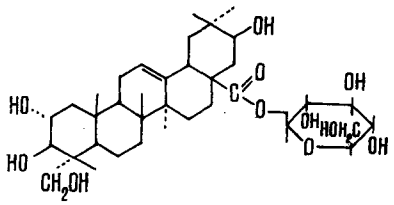
The fractions enriched in triterpenoids were combined, evaporated, and reseparated in the chloroform-methanol–water (65:35:8) system. Two individual substances were obtained in each case. The less polar of them was substance A, with the composition $C_{30}H_{48}O_6$, mp 266-269°C, $[\alpha]_D^{20}+26.0\pm2.0°$ (c 0.96; CH_3OH), M^+ 504 (mass spectrometry). The nature of the absorption curve in the 1200-1200-cm^{-1} region of the IR spectrum enables this compound to be assigned to triterpenoids of the β-amyrin series [2].

The methylation of substance A with diazomethane gave its monomethyl ester $C_{31}H_{50}O_6$, mp 270°C (decomp.), the mass spectrum of which had the peaks of ions with m/e: 518 (M^+), 500, 458, 440, 278, 260, 246, 219, 218, 205, 201, 200, 133. All these facts correspond to the triterpenoid sapogenin – caccigenin (2α, 3β, 21β,23-tetrahydroxyolean-12-ene-28-oic acid) isolated from Caccinia glauca Savi (family Boraginaceae) [3]. The monomethyl ester of substance A was chromatographically identical with the methyl ester of caccigenin kindly provided by Professor Rangaswami (University of Delhi, India).

Substance B proved to be a glycoside, and we have called it poterioside, $C_{96}H_{58}O_{11}$, mp 270-279°C (decomp.), $[\alpha]_D^{20}+38.4\pm2.0°$ (c 1.04; CH_3OH). Poterioside was hydrolyzed with 5% H_2SO_4 at 100°C for 5 h. The aglycone was isolated and was found to be identical with caccigenin. D-Glucose was detected in the hydrolyzate by chromatography in a thin layer of silica gel (TLC) impregnated with a 0.3 M solution of NaH_2PO_4 [4] in the butan-1-ol–methanol–water (5:3:1) system. Similar results were obtained by the hydrolysis of poterioside with the enzymes of the grape snail Helix plectotropis (35°C, 2 days).

Saponification of the glycoside with 10% ethanolic KOH also yielded the aglycone, which shows that the carbohydrate residue is attached to the carboxy group of the aglycone at C_{17}.

After the cleavage of the permethylate of poterioside with 5% HCl, 2,3,4,6-tetra-O-methyl-D-glucose was identified by TLC in the benzene–acetone (2:1) system, from which it follows that the glycoside contains only one molecule of glucose.



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The β-configuration of the glycosidic center was found from the difference in the molecular rotations of poterioside and the aglycone. Consequently, poterioside has the above structure.

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